Trapping by Di-*tert*-butyl Selenoketone of the Biradicals Produced in the Photochemistry of Phenyl Alkyl Ketones. A Kinetic Study

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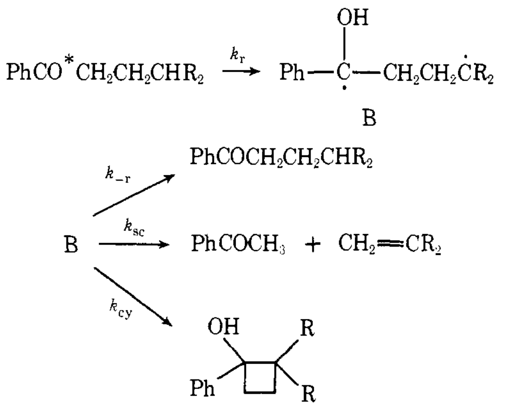
Contribution from the Radiation Laboratory,[1] University of Notre Dame, Notre Dame, Indiana 46556. *Received October 25, 1976*

Abstract: UV irradiation of butyrophenone, valerophenone, and γ-methylvalerophenone in the presence of di-*tert*-butyl selenoketone results in the consumption of the latter via biradical trapping. Quantum yields of up to 0.21 have been observed for valerophenone in benzene. In the presence of *tert*-butyl alcohol the quantum yields of biradical trapping are enhanced as a result of the increase in biradical lifetimes. The products of the reaction have the structure: $PhCOCH_2CH_2C^1R^2RSeC(Bu^t)_2H$ (^1R, ^2R = H, Me) and result from intramolecular hydrogen transfer in the intermediate 1,6-biradical generated in the trapping step. Di-*tert*-butyl selenoketone is a diffusion-controlled triplet quencher. The efficiency of trapping is higher in high viscosity solvents (e.g., tetradecane) as a result of a decrease in the rate constant for triplet quenching. The reaction of the selenoketone with 1,4-biradicals seems to be quite general and has considerably less kinetic restrictions than previously reported techniques for the study of these biradicals.

The Norrish type II reaction in phenyl alkyl ketones has been extensively studied.[2] The mechanism of the reaction, as well as the factors which determine the kinetics of the intramolecular hydrogen abstraction leading to the intermediate biradical, are fairly well understood.

The quantum yields of product formation, as well as their temperature and solvent dependence, are usually determined solely by the behavior of the intermediate biradical,[3] since, in the absence of quenchers, the quantum yield of biradical production, Φ_B, is 1.

The intermediate biradical, B, has been successfully trapped by thiols,[4] hydrogen bromide,[5] and methylmethacrylate.[6] The interaction of B with good hydrogen bonding solvents (e.g., *tert*-butyl alcohol or pyridine)[2,7] or oxygen[8,9] is known to result in changes in the relative values of k_{-r}, k_{sc}, and k_{cy}.



Wagner and Liu have been able to obtain a reliable lifetime for the biradical produced from α-allylbutyrophenone.[10] All trapping experiments previously reported consistently indicate that triplet-derived type II biradicals have lifetimes in the range of 10^{-5} to 10^{-7} s.

All the experiments mentioned above help to elucidate the behavior of the intermediate biradical but cannot be regarded as general methods, since their applicability is dependent on specific structural characteristics (e.g., α-allylbutyrophenone)[10] or otherwise require a small $k_q\tau$ value for the triplet state (k_q refers to quenching by the biradical trap).

The recently prepared di-*tert*-butyl selenoketone[11] has been shown to be an efficient spin trap[12,13] for a large number of common free radicals. We report in this paper that the carbon–selenium double bond is an efficient trap for biradicals produced in the Norrish type II reaction. The method, which has been applied to butyrophenone, valerophenone, and γ-methylvalerophenone in several solvents provides a rather general technique for the study of this type of biradicals.

Results

No chemical change is observed when acetophenone is irradiated in the presence of di-*tert*-butyl selenoketone in benzene solvent. Expressed in terms of quantum yield, $\Phi_{-CSe} \ll 0.003$, where Φ_{-CSe} corresponds to selenoketone consumption.

When butyrophenone, valerophenone, or γ-methylvalerophenone are irradiated in the presence of selenoketone, significant consumption of the latter is observed. The quantum yield of the process, Φ_{-CSe}, is larger for the ketones having shorter triplet lifetimes. This can be taken to mean that the consumption of selenoketone is largely determined by the probability of intramolecular abstraction leading to the biradical. These observations constitute strong evidence in favor of biradical participation in the elementary steps leading to selenoketone consumption.[14]

The product of the reaction in the case of γ-methylvalerophenone was identified by NMR, IR, and mass spectroscopy as $PhCOCH_2CH_2C(CH_3)_2SeC(Bu_2^t)H$ and supports the biradical mechanism.

Di-*tert*-butyl selenoketone is expected to have a very low triplet energy (probably $E_T \lesssim 40$ kcal mol^{-1})[15] and therefore should be a diffusion-controlled triplet quencher. This was confirmed in the case of butyrophenone, where the system follows linear Stern–Volmer behavior at low concentrations and conversions, leading to $k_q\tau = 490\ M^{-1}$ in benzene at 32 °C, which agrees with the reported values for 1,3-pentadiene.[1,18,19] We will assume that the $k_q\tau$ value for the selenoketone is the same as for 1,3-pentadiene for all the ketones employed in this study.

Table I gives the quantum yields of selenoketone consumption in benzene solvent for the three ketones examined. Also included is Φ_B which is the probability of biradical production from the triplet state, i.e.

$$\Phi_B = \frac{k_r}{k_r + k_q[Bu_2{}^tCSe]} \qquad (1)$$

Scheme I shows the proposed mechanism for the photochemistry of phenyl alkyl ketones in the presence of di-*tert*-butyl selenoketone.

K stands for the ketone, T for the selenoketone, and ACP

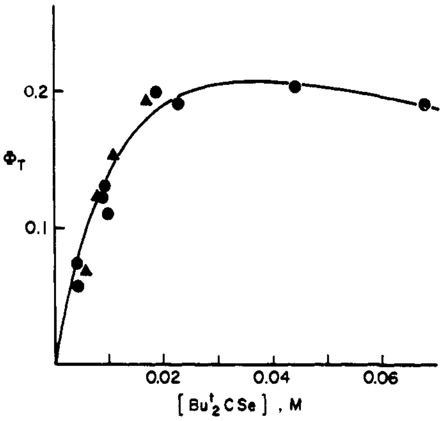


Figure 1. Plot of Φ_T vs. selenoketone concentration for valerophenone in benzene at 32 °C: (●) VPC measurements; (▲) spectrophotometric measurements. The curve has been calculated for $\alpha = 0.045$ M and $\beta = 0.031$ M.

Table I. Photolysis of PhCOR in the Presence of Di-*tert*-butyl Selenoketone in Benzene Solvent at 32 °C

R	[$Bu_2{}^tCSe$], M	Φ_{-CSe}	$\Phi_B{}^a$	log $\tau_T{}^b$
CH_3	0.021	±0.003	0	−5.48[c]
n-C_3H_7	0.021	0.03	0.09	−6.93[d]
n-C_4H_9	0.0045	0.074	0.87	−8.12[d]
	0.021	0.19	0.60	
	0.044	0.21	0.41	
$CH_2CH_2CH(CH_3)_2$	0.021	0.26	0.85	−8.72[d]

[a] Based on β for 1,3-pentadiene.[19] [b] Triplet lifetime in seconds. [c] H. Lutz and L. Lindqvist, *Chem. Commun.*, 493 (1971). [d] Reference 19.

Scheme I

$$K \xrightarrow{h\nu} {}^1K$$

$${}^1K \rightarrow {}^3K$$

$${}^3K \xrightarrow{k_r} B$$

$${}^3K + T \xrightarrow{k_q} K + {}^3T$$

$$B \xrightarrow{k_{sc}} ACP + \text{olefin}$$

$$B \xrightarrow{k_{cy}} \text{cyclobutanol}$$

$$B \xrightarrow{k_{-r}} K$$

$$B + T \xrightarrow{k_T} \cdot BT\cdot \rightarrow \text{products}$$

for acetophenone. The triplet selenoketone, ^3T, probably decays by self-quenching in a reaction similar to the well-documented self-quenching of thioketones.[20-24]

If we define:

$$\alpha = \frac{k_{sc} + k_{cy} + k_{-r}}{k_T} \tag{2}$$

$$\beta = k_r/k_q \tag{3}$$

then,

$$\Phi_T = \frac{1}{1 + [T]/\beta}\left(\frac{1}{1 + \alpha/[T]}\right) \tag{4}$$

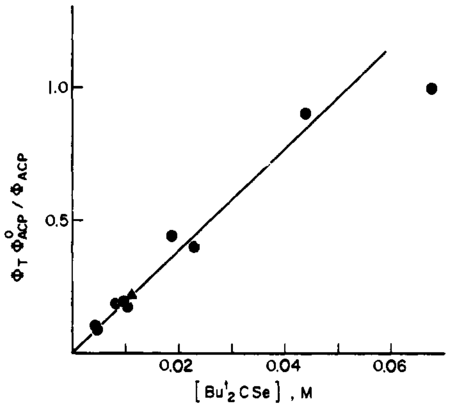


Figure 2. Determination of α using eq 9 for valerophenone in benzene at 32 °C: (●) VPC measurements; (▲) spectrophotometric measurement of the selenoketone.

The plot of Φ_T vs. [T] is expected to show a maximum. Derivation of eq 4 with respect to [T] gives the conditions at that maximum:

$$\Phi_T{}^{max} = \left(\frac{1}{1 + \sqrt{\frac{\alpha}{\beta}}}\right)^2 \tag{5}$$

$$[T]^{max} = (\alpha\beta)^{1/2} \tag{6}$$

$$\Phi_B{}^{max} = (\Phi_T{}^{max})^{1/2} \tag{7}$$

and

$$\frac{1}{1 + [T]/\beta} = \frac{1}{1 + \alpha/[T]} \tag{8}$$

Figure 1 shows the dependence of Φ_T with [T] for valerophenone in benzene. The curve has been calculated using $\alpha = 0.045$ M and $\beta = 0.031$ M, the latter being obtained from the quenching data for 1,3-pentadiene.

Figure 2 shows a linear plot of the results for valerophenone in benzene at 32 °C, using the following equation:

$$\frac{\Phi_T\Phi^0{}_{ACP}}{\Phi_{ACP}} = \frac{[T]}{\alpha} \tag{9}$$

The slope in Figure 2 corresponds to $\alpha = 0.052$ M, in reasonable agreement with Figure 1. We note that the quantum yields of acetophenone production at high selenoketone concentrations are subject to larger errors than in the low concentration region (see Experimental Section).

Stern–Volmer plots for systems involving quenching of the triplet state and scavenging of the biradical are expected to show curvature, since $\Phi^0{}_{ACP}/\Phi_{ACP}$ is a quadratic function of the concentration of T:

$$\frac{\Phi^0{}_{ACP}}{\Phi_{ACP}} = 1 + \left(\frac{1}{\alpha} + \frac{1}{\beta}\right)[T] + \frac{[T]^2}{\alpha\beta} \tag{10}$$

The plot becomes linear only when the last term in eq 10 can be neglected. We note at this point that the slope of the Stern–Volmer plot for butyrophenone mentioned above corresponds to $(1/\alpha + 1/\beta)$ rather than to $1/\beta$ as usual; however, the value of β is over twenty times smaller than the value of α for this ketone and should not affect our conclusion that the quenching of phenyl alkyl ketones by the selenoketone is diffusion controlled.

In principle, α and β can both be obtained by studying the quantum yields of acetophenone formation as a function of biradical-trap concentration, that is, determining the coefficients of eq 10. Unfortunately, measuring the curvature of Stern–Volmer plots is not easy, since even a relatively small dispersion of the experimental data can easily mask the results. Figure 3 shows a Stern–Volmer plot for valerophenone in

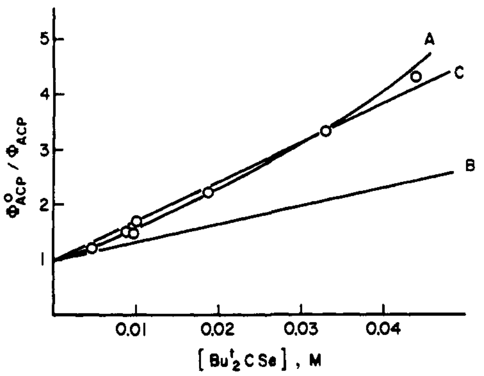


Figure 3. Stern-Volmer plot for valerophenone in benzene at 32 °C: (A) best quadratic fit using eq 10 with $\alpha = 0.051$ M and $\beta = 0.031$ M; (B) calculated line using eq 12; (C) best linear fit.

benzene. Curve A corresponds to the best fit for a quadratic equation, taking $\beta = 0.031$ M and optimizing α, to give $\alpha = 0.051$ M. Curve B corresponds to the slope expected if k_q is calculated from the experiments with butyrophenone, i.e.

$$(k_q\tau)_{VLP} = (k_q\tau)_{BTP}\,(\tau_{VLP}/\tau_{BTP}) \tag{11}$$

where the subindices BTP and VLP stand for butyrophenone and valerophenone, respectively. The line C corresponds to the best linear fit of the data. We note that although the quadratic fit A is better than C, the latter is not unsatisfactory.

We have only included in Figure 3 data obtained under optimum conditions, i.e., low conversions and avoiding high selenoketone concentrations (see Experimental Section). Each point is the average of three chromatographic measurements.

Figure 4 shows a typical plot of concentration of selenoketone as a function of time for $I_a = 4.67 \times 10^{-6}$ einstein l.$^{-1}$ s^{-1}. It should be noted that the change in slope is very slow; in other words, the overall order with [T] is well below 1. The change in slope is consistent with the assumption that the products of the reaction are not efficient triplet quenchers.[25] From the point of view of the application of the method to the study of biradicals, it means that in the measurement of quantum yields at conversions in the range of 10-20%, the error introduced resulting from nonlinearity of the consumption curve is very small. All the concentrations of selenoketone given in the tables are average between the initial and final value.

Solvent Effects. Hydroxylic solvents, in particular *tert*-butyl alcohol, are known to increase the quantum yields of photofragmentation and photocyclization.[2,7] The effect is supposed to result from a marked decrease of k_{-r} due to hydrogen bonding. The three ketones used in this work have been reported to have unity limiting quantum yields.[26] The quantum yields of fragmentation plus cyclization in benzene (subindex zero) and in a given solvent (subindex one) and the corresponding biradical lifetimes are directly related:

$$\tau_B{}^1/\tau_B{}^0 = \Phi_1/\Phi_0 \tag{12}$$

We believe that the changes in Φ_{-CSe} reflect the same phenomena. That is, the rate of reaction of the biradical with the selenoketone is not expected to be very solvent dependent; therefore, the change in α is a direct measure of the change in biradical lifetimes. The results for valerophenone in benzene and 2 M *tert*-butyl alcohol in benzene are included in Table II. A similar effect is observed with the other ketones (see Discussion).

A different type of behavior is observed when nonhydroxylic solvents of different viscosity are used. For example, Φ_{-CSe} is different in cyclopentane, benzene, and tetradecane (see Table II). The change results mainly from changes in Φ_B caused by variations in the rate of diffusion.

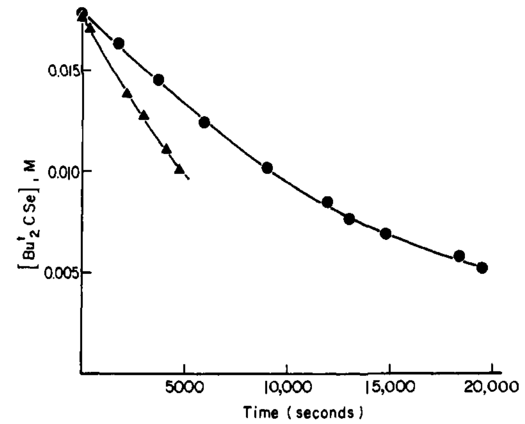


Figure 4. Consumption of selenoketone for $I_a = 4.67 \times 10^{-6}$ einstein l.$^{-1}$ s^{-1} for valerophenone at 32 °C: (●) benzene solvent; (▲) 2 M *tert*-butyl alcohol in benzene.

Table II. Solvent Effects on the Photochemistry of the Valerophenone-Di-*tert*-butyl Selenoketone System at 32 °C

Solvent	[Bu$_2{}^t$CSe], M	Φ_{-CSe}	(Φ_{-CSe}-Φ^0_{ACP})/ Φ_{ACP}	(Φ_{-CSe})^a 0.01 M	η
Benzene	0.0088	0.12	0.18	0.13	0.54
2 M Bu^{t}OH/ benzene	0.0077	0.17	0.40	0.20	
Cyclopentane	0.0088	0.09	0.16	0.10	0.40
Tetradecane	0.010	0.18	0.25	0.18	2.04

[a] Estimated for 0.01 M selenoketone using the equation: $\Phi_{-CSe}/\Phi_{-CSe}{}' \simeq (1 + \alpha/[T]')/(1 + \alpha/[T])$ which assumes that $[T]/\beta \ll 1$, a condition which is normally met in this concentration range; α was calculated from columns 2 and 4 in this table.

Discussion

The results in Table I constitute strong evidence in favor of a biradical reaction. If the reaction involved a triplet state process we would expect to observe the highest quantum yield for acetophenone because of its comparatively long triplet lifetime.[27] On the contrary, we observe that Φ_{-CSe} increases with increasing Φ_B. For 0.021 M selenoketone in benzene, approximately one-third of the biradicals are trapped in all cases.

Further support for a biradical mechanism is provided by the viscosity dependence of Φ_{-CSe}. In the case of a triplet state reaction the quantum yields would be expected to be lower in high viscosity solvents (see Table II).

In Figure 1 we have equated Φ_T to Φ_{-CSe}. For this assumption to be correct the biradical B has to undergo addition to the selenoketone at only one end. Three reasons support this assumption: (a) the final product contains only one selenoketone moiety; (b) the assumption is consistent with the stoichiometry observed (see Experimental Section); and (c) the position of the maximum in Figure 1 agrees with:

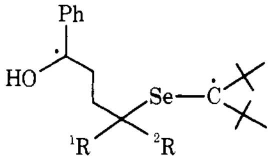
$$\Phi_T{}^{max} = \left[\frac{1}{1 + \dfrac{[T]^{max}}{\beta}}\right]^2 \tag{13}$$

which is based on the assumption mentioned above.

We conclude that only one end of the biradical reacts with the selenoketone. From the evidence in the case of free radical additions[12,13] it seems certain that the alkyl end must be the reactive one. Further support for this conclusion was obtained from the photolysis of the benzophenone-benzhydrol system

(0.2 M in each component) in the presence of 0.012 M selenoketone. Under these conditions less than 1.5% of the ketyl radicals produced were trapped, if any at all. This selenoketone concentration traps about 20% of the biradicals generated from any of the ketones having γ-hydrogens. We note that the ketyl radicals have under our experimental conditions a lifetime at least 10^4 times longer than the 1,4-biradicals, mainly as a result of their bimolecular decay.

From the preceding discussion we conclude that the biradical ·BT· (Scheme I) has the following structure:



(·BT·)

^{1}R, ^{2}R = H, Me

The ultimate fate of these biradicals is not directly relevant to the kinetics of the processes in Scheme I. Nevertheless, the question of their behavior is an interesting one. Our product studies indicate that the major route of decay of ·BT· is by intramolecular transfer of the hydroxylic hydrogen to give $PhCOCH_2CH_2C^1R^2RSe(Bu^t)_2H$. The reaction is about 45-50 kcal mol^{-1} exothermic and probably has a low activation energy.

As pointed out above, α and β can be obtained from the Stern-Volmer plot (Figure 3 and eq 10). Unfortunately, the method is quite unreliable, and even when α and β are of similar magnitude (e.g., valerophenone), the curvature is not necessarily obvious. We would like to emphasize at this stage that a "reasonable" linear fit does not prove by itself the absence of biradical trapping. In fact, the quantum yield of fragmentation is not a good monitor for biradical processes, unless k_q is relatively small, as has been shown to be the case with thiols.[4,28] The difference in slopes of curves A and line B in Figure 3 reflects the effect of biradical trapping on Φ_{ACP}.

Values of α can be calculated by four different methods: (i) by fitting the Φ_{-CSe} vs. [T] curve, Figure 1 and eq 4; (ii) plotting $[\Phi_{-CSe}\Phi^0{}_{ACP}/\Phi_{ACP}]$ vs. [T], Figure 2 and eq 9; (iii) measuring Φ_{-CSe} at a given selenoketone concentration and calculating Φ_B using eq 1, then

$$\alpha = [T]\left(\frac{\Phi_B}{\Phi_{-CSe}} - 1\right) \qquad (14)$$

and (iv) fitting the Stern-Volmer plot to eq 10. We have avoided using method iv because of the reasons given above.

Method iii is by far the simplest one and gives reproducible results provided that (Φ_B/Φ_{-CSe}) is not very close to one.

Table III gives a summary of values of α obtained using the different methods.

The values of α for the three ketones in benzene are essentially the same, meaning that the intramolecular reactivity is determined by the same parameters which determine the intermolecular reactivity. From the extremely facile addition of numerous free radicals to the selenoketone,[12,13] it seems reasonable to assume that k_T is not very dependent upon the stability of the reactive free radical center. Therefore, the biradicals from butyrophenone, valerophenone, and γ-methylvalerophenone must have very similar lifetimes. Unfortunately, no measurements have been reported of rates of free radical additions to the selenoketone; however, from the observation that the selenoketone is a better spin trap than di-*tert*-butyl thioketone,[29] we believe that k_T is probably around 5×10^7 M^{-1} s^{-1} at room temperature. Our biradical lifetimes based on this value are ca. 4×10^{-7} s in benzene.

The fact that the selenoketone is an unreactive diffusion-controlled quencher of carbonyl triplets can be considered to be an advantage, since it allows the easy estimation of $k_q[T]$ and therefore of Φ_B. We note that method iii (see above) is based on this property and cannot be applied to other systems where k_q is smaller and more likely to be subject to fluctuations.

Table III. Biradical Reactivities at 32 °C

Ketone	Solvent	α, M	Method[a]
Butyrophenone	Benzene	0.056	ii
	Benzene	0.042	iii
	Bu^tOH, 2 M[b]	0.027	ii
	Bu^tOH; 2 M[b]	(0.003)[c]	iii
Valerophenone	Benzene	0.045	i
	Benzene	0.052	ii
	Benzene	0.045	iii
	Cyclopentane	0.054	ii
	Cyclopentane	0.060	iii[d]
	Tetradecane	0.041	ii
	Tetradecane	0.042	iii[d]
	Bu^tCH, 2 M[b]	0.019	ii
	Bu^tOH, 2 M[b]	0.027	iii
γ-Methylvalerophenone	Benzene	0.048	iii
	Bu^tOH, 2 M[b]	0.019	iii

[a] See text. [b] In benzene. [c] Φ_B/Φ_{-CSe} too close to 1 (see eq 14). [d] Assuming that k_{diff} is inversely proportional to η, see Table II.

The values of α in Table III indicate that the lifetime of the biradical from valerophenone is 2.1 times longer in 2 M *tert*-butyl alcohol than in benzene. A similar value can be calculated from the changes in $\Phi^0{}_{ACP}$ in the two solvents (eq 12). From Wagner's data[3] we estimate a ratio of lifetimes of 2.7.

The observation that Φ_{-CSe} increases with increasing solvent viscosity is not surprising. It reflects changes in k_q and provides further support for the mechanism of Scheme I. The values of α show a decreasing trend with increasing viscosity. This cannot reflect higher values of k_T at higher viscosities. We believe that the explanation for the dependence of α on viscosity must be attributed to a small increase of the biradical lifetimes in high viscosity solvents; this increase in lifetime reflecting a slowdown in molecular motions.

In conclusion, we believe that the reaction described in this paper can have rather general applicability to a variety of systems which involve, or are presumed to involve, biradicals. Even the ketones having relatively high $k_q\tau$ values (e.g., butyrophenone) can be examined by this technique.

Finally, we note type II biradicals undergo a number of intermolecular reactions as shown in this and previous studies.[2,4-9] The assumption that type II biradicals undergo *only* intramolecular reactions has been a common one, in particular in the case of polymer photodegradation where the Norrish type II process is known to play an important role.[31] The question remains as to whether this assumption is correct, particularly when molecules of high reactivity toward free radical centers are of common use in polymer chemistry. This question becomes even more important in the light of our observation that biradical trapping is enhanced in high viscosity media.

Experimental Section

Materials. Di-*tert*-butyl selenoketone was prepared by reaction of di-*tert*-butyl ketone triphenylphosphoranylidene hydrazone with selenium metal.[11,13] It was purified by vacuum distillation. The amount used in each experiment or series of experiments was trap-to-trap distilled under high vacuum in a mercury-free, grease-free system immediately before it was used. This procedure eliminates any impurity (polymer?) which produces a considerable red shift in the UV cut-off. All concentrations given in this paper are based on ϵ = 21 at 690 nm.

Butyrophenone, valerophenone, and acetophenone (Aldrich) were distilled prior to use. γ-Methylvalerophenone (Fluka) was a generous gift from Dr. K. U. Ingold and was distilled twice. Benzene (Fisher, certified ACS) was used as received, and *tert*-butyl alcohol (Baker) was found to have a quenching impurity and was recrystallized ten times.

Undecane, dodecane (used as internal standards), and tetradecane were Polyscience Corp. products. Cyclopentane was a product of Phillips Petroleum Co.

Irradiation. Two optical systems were used: (A) a static system using a B & L SP-200 mercury lamp with an optical filter (T_{max} at 368 nm, bandwidth 10 nm); the sample was contained in a 1-cm path quartz spectrophotometer cell; or (B) a Rayonet reactor fitted with a merry-go-round and sixteen RPR-3500 lamps. The samples were contained in matched Pyrex tubes (9 mm o.d.).

Sample Preparation and Analysis. Samples irradiated in optical system A were examined periodically by absorption spectrophotometry at 690 nm using a Cary-14 spectrophotometer. At the end of each run they were also examined by VPC (6 ft. 5% DC-11 silicone oil on Chromosorb W). This measurement provided average values for Φ_{ACP} and Φ_{-CSe}. Typical radiation doses were of the order of 4.7×10^{-6} einstein $l.^{-1}\ s^{-1}$. The samples were under argon atmosphere.

When the Rayonet reactor was used the samples were degassed by three thaw and freeze cycles. Typical radiation doses were of the order of 7.3×10^{-5} einstein $l.^{-1}\ s^{-1}$. The samples were analyzed by VPC using undecane and dodecane as internal standards for acetophenone and di-*tert*-butyl selenoketone, respectively. The samples containing large selenoketone concentrations (>0.04 M) required the measurement of very small acetophenone-to-selenoketone ratios. In these cases Φ_{ACP} was subject to considerable error (normally in excess).

Actinometry. The photolysis of valerophenone in benzene at 32 °C was used as an actinometer taking $\Phi^0_{ACP} = 0.30$.[3]

Product Studies. These were examined in the case of γ-methylvalerophenone. The choice reflects the high yield of trapping in this system, as well as the relative simplicity of the NMR spectra. The experiments were carried out in benzene-d_6 using an excess of selenoketone. Only one major product is formed. After the samples were irradiated (RPR—3500 lamps) long enough to decompose all the γ-methylvalerophenone (checked by VPC), the solvent and all volatile products (including acetophenone and the excess selenoketone) were eliminated under high vacuum. The sample was then redissolved and examined by NMR (Varian XL-100). The spectrum is consistent with the structure $PhCOCH_2CH_2C(CH_3)_2Se(Bu^t)_2H$ showing δ 7.9 (complex, 2 H, phenyl), 7.1 (complex, 3 H, phenyl), 3.05 (t, 2 H, $-CH_2CO-$), 2.11 (t, 2 H, CH_2), 1.30 (s, 6 H, CMe_2), and 1.22 (s, 18 H, $CBu_2{}^t$). The chemical shift for the hydrogen atom in the di-*tert*-butyl methyl group could not be conclusively established; two singlets at δ 2.60 and 3.54 were observed, one of them probably being due to an impurity (see below). The IR spectra (film) shows 693 s, 745 s, 1115 m, 1220 m, 1220 m, 1270 w, 1365 m, 1465 m, 1690 s (C=O), and 3010 s (wave numbers). The mass spectrum shows peaks at 382 (M^+, Se^{80}), 256, 239, 208, 175 (base), 105, the first four having the isotopic satellite distribution characteristic of selenium. The spectrum was obtained at 115 °C, this being the lowest temperature at which the product has sufficient vapor pressure. At higher temperatures, or prolonged heating at 115 °C, extensive thermal decomposition occurs, leading to mass peaks at 208, 174 (base), 159, 105.

An impurity, light yellow in color, is generated toward the end of the reaction. This probably arises from photodecomposition of $PhCOCH_2CH_2C(CH_3)_2Se(Bu^t)_2H$, giving $(Bu^t)_2HSe\cdot$ radicals and ultimately a diselenide, in a mechanism similar to that observed in the photolysis of ketoalkyltrimethylstannanes.[32,33]

According to the mechanism in Scheme I, the following equations should hold:

$$\Phi_p = \Phi_{-CSe} \tag{15}$$

$$\Phi_{-K} = \Phi_{-CSe} + 1.13\Phi_{ACP} \tag{16}$$

where Φ_p is the quantum yield of product formation and the coefficient of 1.13 in eq 16 takes into account cyclobutanol formation in the case of γ-methylvalerophenone.[26,34] Equation 15 was checked by NMR, while eq 16 was shown to account for at least 90% of the ketone consumed by both NMR and VPC.

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References and Notes

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U.S. Energy Research and Development Administration. This is ERDA Document No. NDRL-1701.

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